

5 ELECTROCHEMICAL CELL HAVING A PHYSICAL VAPOR
DEPOSITED ELECTRODE AND METHOD OF MANUFACTURE

CROSS-REFERENCE TO RELATED APPLICATION

10 The present application is a divisional of
application Serial No. 09/498,667, filed February 7,
2000, which claims priority based on provisional
application Serial No. 60/118,977, filed February 8,
1999.

15 BACKGROUND OF THE INVENTION

1. Field Of The Invention

20 The present invention generally relates to the art
of electrical energy storage devices and more
particularly, to an electrode of an electrochemical cell
or capacitor produced by a physical vapor deposition
process.

25 2. Prior Art

Physical vapor plating involves introducing a
material of interest into a vacuum and heating to a
30 temperature at which the material reaches its vapor
pressure. When molecular rays of the vaporized material
attain a sufficient energy such that their mean free
path causes them to impinge upon and precipitate onto a
substrate, a coating of the material is formed. While
35 physical vapor deposition processes are known in the

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5 art, as of yet, they have not been used to deposit an
electrode active material onto a substrate to provide an
electrode component for an electrochemical cell and to
deposit a semiconductive or pseudocapacitive material
10 onto a substrate to provide an electrode component for a
capacitor.

SUMMARY OF THE INVENTION

15 The present invention is directed to a novel and
unique application of the physical vapor deposition
process. The present process provides a coating of an
electrochemically active material on a substrate,
preferably a conductive substrate. The thusly produced
coated substrate is useful as an electrode, for example,
20 a cathode electrode incorporated into a primary
electrochemical cell, and as the anode and/or the
cathode of a secondary electrochemical cell. The
assembly of the cell incorporating the electrode
component made by physical vapor depositing an electrode
25 active material onto a conductive substrate according to
the present invention is preferably in the form of a
wound element cell. That is, the fabricated cathode
together with an anode and a separator are wound
together in a "jellyroll" end type configuration or a
30 "wound element cell stack" such that the anode is on the
outside of the roll to make electrical contact with the
cell case in a case-negative configuration. Other types
of cells such as prismatic, bobbin shape and flat cells
are also possible with the present invention.

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5 In the case of a capacitor, the present physical
vapor deposition process is useful for producing an
anode or a cathode in an electrochemical capacitor or
the cathode in an electrolytic capacitor. Regardless
the type, the capacitor configuration generally includes
10 a substrate of a conductive metal such as titanium or
tantalum provided with a semiconductive or a
pseudocapacitive oxide coating, nitride coating, carbon
nitride coating, or carbide coating.

15 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

One embodiment of the present invention is directed
to the use of a physically vapor deposited coating of an
electrode active material on a conductive substrate to
20 thereby form an electrode component for an
electrochemical cell. In one preferred embodiment, the
electrode active material is a cathode active material
deposited onto a substrate by means of a physical vapor
deposition process to form a cathode component for an
25 electrochemical cell. The cathode active material is
selected from the group consisting of a metal, a metal
oxide, mixed metal oxide, a metal sulfide and a
carbonaceous material, and mixtures thereof. Suitable
cathode materials include silver vanadium oxide, copper
30 silver vanadium oxide, manganese dioxide, titanium
disulfide, copper oxide, cobalt oxide, chromium oxide,
copper sulfide, iron sulfide, iron disulfide, carbon and
fluorinated carbon. The solid cathode exhibits

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5 excellent thermal stability and is generally safer and
less reactive than a non-solid cathode.

Preferably, the solid cathode material comprises a
mixed metal oxide formed by physical vapor depositing
various metal oxides or metal oxide/elemental metal
10 combinations. The materials thereby produced contain
metals and oxides of Groups IB, IIB, IIIB, IVB, VB, VIB,
VIIB and VIII of the Periodic Table of Elements, which
includes the noble metals and/or their oxide compounds.

By way of illustration, and in no way intended to
15 be limiting, an exemplary cathode active material
comprises silver vanadium oxide having the general
formula $Ag_xV_2O_y$ in any one of its many phases, i.e.
 β -phase silver vanadium oxide having in the general
formula $x = 0.35$ and $y = 5.18$, γ -phase silver vanadium
20 oxide having in the general formula $x = 0.74$ and $y =$
 5.37 and ϵ -phase silver vanadium oxide having in the
general formula $x = 1.0$ and $y = 5.5$, and combination and
mixtures of phases thereof. Preferably, the cathode
active material, whether comprised of silver vanadium
25 oxide or a similarly suitable material, is deposited
onto a substrate of titanium, stainless steel, nickel,
tantalum, platinum, gold or aluminum by a physical vapor
deposition process. The thusly formed exemplary
electrode can be incorporated into an alkali metal
30 electrochemical cell, and more particularly, a lithium
electrochemical cell.

Another preferred embodiment of the present
invention comprises coating an alkalated material onto a
conductive substrate of the above described materials by

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5 a physical vapor deposition process to provide a cathode
for a secondary electrochemical cell. For example, in
the case of the alkalated material being a lithiated
material suitable materials include oxides, sulfides,
selenides and tellurides of such metals as vanadium,
10 titanium, chromium, copper, tin, molybdenum, niobium,
iron, nickel, cobalt and manganese. Among the suitable
oxides are LiNiO_2 , LiMn_2O_4 , LiCoO_2 , $\text{LiCo}_{0.92}\text{Sn}_{0.08}\text{O}_2$ and
 $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$. The anode for such a secondary
electrochemical cell can comprise a particulate
15 carbonaceous composition including carbon together with
a filamentary, electrically conductive material such as
carbon black. Accordingly, it is further contemplated
by the scope of the present invention that particulate
carbonaceous compositions are physically vapor deposited
20 onto a conductive substrate for use as an anode
component in a secondary cell and as the cathode in a
primary electrochemical cell.

Physical vapor deposited coatings rely mostly upon
mechanical bonding to the substrate surface. It is,
25 therefore, critical that the electrode substrate be
properly prepared to ensure coating quality. It is
especially necessary that the surface remain
uncontaminated by lubricants from handling equipment or
body oils from the hands. Suitable substrate surface
30 preparation techniques include scraping, wire brushing,
machining, grit blasting, or by chemical action. It
also is recommended that the prepared surface be coated
as soon as possible after preparation to prevent the
possibility of contamination or surface oxidation.

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5 After substrate surface cleaning, surface roughness
is the next most critical factor for properly applying a
physical vapor deposited coating of electrode active
material. Three methods of roughening the electrode
10 rough threading, grit blasting, and a combination of
rough threading, then grit blasting, as are well known
to those skilled in the art of chemical vapor deposition
techniques.

15 According to the present invention any one of the
previously listed electrode active materials including
the enumerated cathode active materials and the
lithiated materials is heated in a vacuum to a
temperature at which the material reaches its vapor
pressure. A suitable vacuum pressure is about 10^{-2} torr
20 (about 10^{-5} atm) or greater. Under such processing
conditions, the vaporized material emits molecular rays
in all directions. The vacuum must be great enough that
the mean free path of the residual gas molecules is
greater than the distance from the material evaporation
25 source to the substrate being coated. Accordingly, the
physical vapor deposition process of the present
invention requires that the molecular vapor travel from
its source to the substrate to form the desired coating
without intermediate collision and precipitation.

30 One of the benefits of the present invention is
that electrode plates made by a physical vapor
deposition process according to the present invention
are thinner than currently available electrodes. This
provides for the manufacture of higher surface area

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5 cells housed in smaller containers than conventional
electrode preparation technology permits. In that
respect, the electrode active material can be coated on
both sides of the substrate by a physical vapor
deposition process to further increase the electrode
10 active surface area. The substrate can also be
perforated so that the coatings on both sides of the
substrate are in physical contact with each other to
lock the electrode active material onto the substrate.

The exemplary cell of the present invention having
15 the cathode component made by the physical vapor
deposition of a cathode active material onto a suitable
substrate and preferably silver vanadium oxide deposited
onto a titanium substrate, further comprises an anode
selected from Group IA of the Periodic Table of
20 Elements, including lithium, sodium, potassium, etc.,
and their alloys and intermetallic compounds including,
for example Li-Si, Li-B and Li-Si-B alloys and
intermetallic compounds. The preferred anode comprises
lithium.

25 The form of the anode may vary, but preferably the
anode is a thin metal sheet or foil of the anode metal,
pressed or rolled on a metallic anode current collector,
i.e., preferably comprising nickel to form an anode
component. In the electrochemical cell of the present
30 invention, the anode component has an extended tab or
lead of the same material as the anode current
collector, i.e., preferably nickel integrally formed
therewith such as by welding and contacted by a weld to
a cell case of conductive metal in a case-negative

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5 electrical configuration. Alternatively, the anode may
be formed in some other geometry, such as a bobbin
shape, cylinder or pellet to allow an alternate low
surface area cell design.

10 The exemplary cell of the present invention having
the cathode component made by physical vapor depositing
a cathode active material onto a suitable substrate
includes a separator to provide physical separation
between the anode and cathode active electrodes. The
separator is of electrically insulative material to
15 prevent an internal electrical short circuit between the
electrodes, and the separator material also is
chemically unreactive with the anode and cathode active
materials and both chemically unreactive with and
insoluble in the electrolyte. In addition, the
20 separator material has a degree of porosity sufficient
to allow flow therethrough of the electrolyte during the
electrochemical reaction of the cell. Illustrative
separator materials include non-woven glass,
polypropylene, polyethylene, glass fiber material,
25 ceramics, a polytetrafluorethylene membrane commercially
available under the designations ZITEX (Chemplast Inc.),
a polypropylene membrane commercially available under
the designation CELGARD (Celanese Plastic Company Inc.)
and DEXIGLAS (C.H. Dexter, Div., Dexter Corp.). Other
30 separator materials that are useful with the present
invention include woven fabric separators comprising
halogenated polymeric fibers, for example of the type
described in U.S. Patent No. 5,415,959 to Pyszczyk et
al., which is assigned to the assignee of the present

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5 invention and incorporated herein be reference. Other
suitable halogenated polymeric materials include, but
are not limited to, polyethylene tetrafluoroethylene
which is commercially available under the name Tefzel, a
trademark of the DuPont Company;
10 polyethylenechlorotrifluoroethylene which is
commercially available under the name Halar, a trademark
of the Allied Chemical Company and polyvinylidene
fluoride.

The form of the separator typically is a sheet
15 which is placed between the anode and cathode electrodes
and in a manner preventing physical contact
therebetween. Such is the case when the anode is folded
in a serpentine-like structure with a plurality of
cathode plates disposed intermediate the anode folds and
20 received in a cell casing or when the electrode
combination is rolled or otherwise formed into a
cylindrical "jellyroll" configuration.

The exemplary electrochemical cell of the present
invention having the cathode component made by physical
25 vapor depositing a cathode active material onto a
suitable substrate further includes a nonaqueous,
ionically conductive electrolyte activating the anode
and the cathode electrodes. The electrolyte serves as a
medium for migration of ions between the anode and the
30 cathode during the electrochemical reactions of the
cell. The electrochemical reactions at the electrodes
involves conversion of the migrating ions into atomic or
molecular forms. Thus, nonaqueous electrolytes suitable
for the present invention are substantially inert to the

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5 anode and cathode materials, and they exhibit those physical properties necessary for ionic transport, namely, low viscosity, low surface tension and wettability.

10 A suitable electrolyte has an inorganic, ionically conductive salt dissolved in a nonaqueous solvent, and more preferably, the electrolyte includes an ionizable alkali metal salt dissolved in a mixture of aprotic organic solvents comprising a low viscosity solvent and a high permittivity solvent. The ionically conductive
15 salt serves as the vehicle for migration of the anode ions to intercalate or react with the cathode active material. In a solid cathode/electrolyte system, the preferred ion-forming alkali metal salt is similar to the alkali metal comprising the anode. Examples of
20 salts useful with the present invention include LiPF_6 , LiAsF_6 , LiSbF_6 , LiBF_4 , LiAlCl_4 , LiNO_3 , LiGaCl_4 , LiSO_3F , $\text{LiB}(\text{C}_6\text{H}_5)_4$, LiClO_4 , $\text{LiC}(\text{SO}_2\text{CF}_3)_3$, LiSCN , $\text{LiO}_3\text{SCF}_2\text{CF}_3$, LiO_2 , $\text{LiC}_6\text{F}_5\text{SO}_3$, LiO_2CCF_3 , $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ and LiCF_3SO_3 , and mixtures thereof.

25 Low viscosity solvents include tetrahydrofuran (THF), methyl acetate (MA), diglyme, triglyme, tetraglyme, dimethyl carbonate (DMC), 1,2-dimethoxyethane (DME), diethyl carbonate, diisopropylether, 1,2-diethoxyethane (DEE), 1-ethoxy,2-
30 methoxyethane (EME), dipropyl carbonate (DPC), ethylmethyl carbonate (EMC), methylpropyl carbonate (MPC) and ethylpropyl carbonate (EPC), and mixtures thereof, and high permittivity solvents include cyclic carbonates, cyclic esters and cyclic amides such as

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5 propylene carbonate (PC), butylene carbonate (BC),
ethylene carbonate (EC), acetonitrile, dimethyl
sulfoxide, dimethyl formamide, dimethyl acetamide,
γ-valerolactone, γ-butyrolactone (GBL) and N-methyl-
pyrrolidinone (NMP) and mixtures thereof. In the
10 preferred electrochemical cell comprising the Li/SVO or
the Li/CSVO couple, the preferred electrolyte is 1.0M to
1.4M LiPF_6 or LiAsF_6 in a 50:50 mixture, by volume, of PC
and DME.

One preferred form of the cell assembly described
15 herein is referred to as a wound element cell. That is,
the fabricated cathode, anode and separator are wound
together in a "jellyroll" end type configuration or
"wound element cell stack" such that the anode is on the
outside of the roll to make electrical contact with the
20 cell case in a case negative configuration. Using
suitable top and bottom insulators, the wound cell stack
is inserted into a metallic case of a suitable size
dimension. The metallic case may comprise materials
such as stainless steel, mild steel, nickel-plated mild
25 steel, titanium or aluminum, but not limited thereto, so
long as the metallic material is compatible for use with
components of the cell.

The cell header comprises a metallic disc-shaped
body with a first hole to accommodate a glass-to-metal
30 seal/terminal pin feedthrough and a hole for electrolyte
filling. The glass used is of a corrosion resistant
type having from between about 0% to about 50% by weight
silicon such as CABAL 12, TA 23 or FUSITE 425 or FUSITE
435. The positive terminal pin feedthrough preferably

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5 comprises titanium although molybdenum and aluminum can
also be used. The cell header comprises elements having
compatibility with the other components of the
electrochemical cell and is resistant to corrosion. The
cathode lead is welded to the positive terminal pin in
10 the glass-to-metal seal and the header is welded to the
case containing the electrode stack. The cell is
thereafter filled with the electrolyte described
hereinabove and hermetically sealed such as by
close-welding a stainless steel ball over the fill hole,
15 but not limited thereto. This above assembly describes
a case negative cell which is the preferred construction
of the exemplary cell of the present invention. As is
well known to those skilled in the art, the exemplary
electrochemical system of the present invention can also
20 be constructed in a case positive configuration.

Another embodiment of the present invention is
directed to the use of a physically vapor deposited
coating of a semiconductive or pseudocapacitive oxide
coating, nitride coating, carbon nitride coating, or
25 carbide coating. The coating is deposited on a
substrate of a conductive metal such as titanium,
molybdenum, tantalum, niobium, cobalt, nickel, stainless
steel, tungsten, platinum, palladium, gold, silver,
copper, chromium, vanadium, aluminum, zirconium,
30 hafnium, zinc and iron, and mixtures and alloys thereof.
The semiconductive or pseudocapacitive material includes
an oxide of a first metal, or a precursor thereof, the
nitride of the first metal, or a precursor thereof, the
carbon nitride of the first metal, or a precursor

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5 thereof, and/or the carbide of the first metal, or a
precursor thereof, the oxide, nitride, carbon nitride
and carbide of the first metal having pseudocapacitive
properties. The first metal is preferably selected from
the group consisting of ruthenium, cobalt, manganese,
10 molybdenum, tungsten, tantalum, iron, niobium, iridium,
titanium, zirconium, hafnium, rhodium, vanadium, osmium,
palladium, platinum, and nickel.

The porous coating may also include a second or
more metals. The second metal is in the form of an
15 oxide, a nitride, a carbon nitride or a carbide, or
precursors thereof and is not essential to the intended
use of the coated foil as a capacitor electrode and the
like. The second metal is different than the first
metal and is selected from one or more of the group
20 consisting of tantalum, titanium, nickel, iridium,
platinum, palladium, gold, silver, cobalt, molybdenum,
ruthenium, manganese, tungsten, iron, zirconium,
hafnium, rhodium, vanadium, osmium, and niobium. In a
preferred embodiment of the invention, the porous
25 coating includes oxides or ruthenium and tantalum, or
precursors thereof.

The thusly fabricated semiconductive or
pseudocapacitive coated substrates are useful as an
anode or a cathode in an electrochemical capacitor or
30 the cathode in an electrolytic capacitor. For
additional disclosure directed to such capacitors,
reference is made to U.S. Patent No. 5,926,362 to
Muffoletto et al., which is assigned to the assignee of
the present invention and incorporated herein by

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5 reference. For a more thorough understanding of the
chemical vapor deposition process, reference is made to
the book Vapor Deposition, edited by Carroll F. Powell,
Joseph H. Oxley and John M. Blocker, Jr. of the Battelle
Memorial Institute, Columbus, Ohio, published by John
10 Wiley & Sons, Inc., the disclosure of which is
incorporated herein by reference.

It is appreciated that various modifications to the
invention concepts described herein may be apparent to
those skilled in the art without departing from the
15 spirit and the scope of the present invention defined by
the hereinafter appended claims.

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